Glass and Ceramics, Vol. 71, Nos. 1 – 2, May, 2014 (Russian Original, Nos. 1 – 2, January – February, 2014)

SCIENCE FOR GLASS PRODUCTION

UDC 666.1:535.372

NEW LUMINESCING OXYFLUORIDE GLASS WITH EUROPIUM AND YTTERBIUM IONS

P. A. Loiko,[1] G. E. Rachkovskaya,[2] G. B. Zakharevich,[2] and K. V. Yumashev[1]

Translated from *Steklo i Keramika*, No. 2, pp. 3 – 6, February, 2014.

New oxyfluoride glasses containing Eu^{3+} and Yb^{3+} have been synthesized in the system SiO_2–PbO–PbF_2–CdF_2 and their physical-chemical properties and the optical absorption and up-conversion of luminescence have been studied. Intense orange-red luminescence (color coordinates $x = 0.64$, $y = 0.36$) peaking near 612 nm was obtained by excitation in the IR range by a commercially available laser diode. This glass is promising for obtaining nano-phase luminescing glass-ceramics for use in up-conversion luminophores and solid-state lasers.

Key words: glass, rare-earth ions, optical absorption, up-conversion, luminescence, nano-phase glass ceramic.

Oxyfluoride glasses and transparent nano-phase glass ceramics containing rare-earth ions, such as erbium, ytterbium, europium, thulium, holmium and praseodymium ions, are promising optical media for use in modern photonics [1 – 3]. Such materials combine attractive spectroscopic properties of low-phonon fluoride materials on the one hand and the production simplicity, high chemical stability, mechanical strength and optical quality of oxide materials on the other [4]. The low energy of the matrix phonons (vibrations) lowers the probability of nonradiative relaxation from an excited state, as a result of which luminescence, including up-conversion, is highly efficient [5]. An entire series of oxyfluoride glass materials suitable for forming (by heating the initial glass) nanosize crystals with the chemical formula LnF_3 (*Ln* = La, Y, Gd) [6, 7] or MF_2 (*M* = Pb, Cd, Sr, Ba) in the glass matrix has been proposed [8]. These materials are used in the producing optical amplifiers for fiber telecommunication systems, luminophores, sources of 'white' light based on LEDs, temperature sensors and up-conversion lasers [9].

Up-conversion is a process where the absorption of two or more photons results in light emission at a wavelength shorter than that of the exciting light. In the process of successive absorption of photons an active ion transitions into a high-lying excited state. Such excitation can occur by means of three basic processes: energy transfer, absorption from an excited state and cross-relaxation. Specifically, in the first case the electronic-excitation energy is transferred from the auxiliary ion (sensitizer) to the emitting ion. This process can be highly efficient for the pair Yb^{3+}–REE^{3+}, where REE^{3+} is a trivalent rare-earth ion with a developed energy-level structure. The most common REE^{3+} ions are Er^{3+}, Tm^{3+}, Ho^{3+} and Pr^{3+} [1 – 5]. The pair Yb^{3+}–REE^{3+} makes it possible to convert the infrared radiation of laser diodes into visible light.

A new oxyfluoride glass in the system SiO_2–PbO–PbF_2–CdF_2 co-activated by europium Eu^{3+} and ytterbium Yb^{3+} ions was chosen as the object of study in the present work. Such glass has a good potential for the production of transparent luminescing glass ceramics containing the nanocrystalline phase REE^{3+}:(Pb, Cd)F_2 [8, 10]. Activation by europium ions Eu^{3+} makes such glass and glass ceramics attractive for developing luminophores for 'white' light-emitting diodes and red up-conversion lasers, while activation by ytterbium ions Yb^{3+} makes it possible to excite visible luminescence by means of commercially available InGaAS semiconductor laser diodes.

The initial glass in the system SiO_2–PbO–PbF_2–CdF_2 was synthesized by the conventional glass technology. The following chemical reagents were used as raw materials: amorphous silicon dioxide, lead oxide and lead and cadmium

[1] Belorussian National Technical University, National Research Center for Optical Materials and Technologies, Minsk, Republic of Belarus.
[2] Belorussian State Technological University, Minsk, Republic of Belarus.
[3] E-mail: rach_halina@mail.ru.

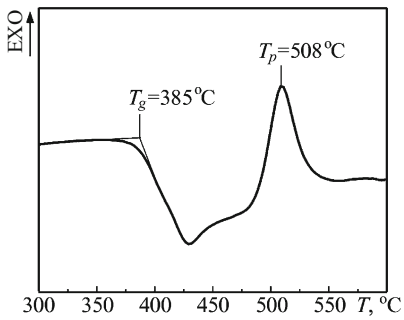

Fig. 1. Differential scanning calorimetry curve for oxyfluoride in the system SiO_2–PbO–PbF_2–CdF_2.

fluorides. The main glass matrix was activated by europium oxide Eu_2O_3 and ytterbium fluoride YbF_3 taken in a 1 : 1 ratio (molar content, %). The components of the batch were carefully mixed and placed in 20 ml corundum crucibles. The glass was synthesized at 900 ± 50 °C in an electric furnace in air in 0.5 h. The ready molten glass was extracted onto a smooth metal surface or into a metal mold, after which the glass was annealed at temperature 300°C in an electric muffle furnace and then allowed to cool to room temperature. The glass samples obtained had a yellow hue.

The main physical-chemical and optical properties of the synthesized glass were studied: softening temperature, linear thermal expansion coefficient (CLTE), density, microhardness, index of refraction, coefficient of absorption at wavelength 960 nm and color index. The concentration of the ions Eu^{3+} and Yb^{3+} in the glass matrix was calculated.

Basic Properties of Oxyfluoride Glass with Eu^{3+} and Yb^{3+} Ions

Synthesis temperature, °C	900 ± 50
Softening temperature, °C	380 ± 5
Density ρ, kg/m³	5260
CLTE, 10^{-7} K^{-1}	103
Microhardness *H*, MPa	3553.9
Refractive index *n*	1.60
Eu^{3+} concentration N_{Eu}, $\times 10^{-20}$ cm^{-3}	2.4
Yb^{3+} concentration N_{Yb}, $\times 10^{-20}$ cm^{-3}	1.2
Absorption coefficient α_{abs} at wavelength 960 nm, cm^{-1}	0.8
Color index (CIE)	Orange-red

Differential scanning calorimetry performed on the samples (Fig. 1) showed that the synthesized oxyfluoride glass co-activated by europium and ytterbium ions is characterized by the glass-forming temperature $T_g = 385$°C. An exothermal peak associated with the precipitation of a crystalline phase is observed at 508°C (T_p). The relatively large value of the thermal stability factor of the glass ($\Delta = T_p - T_g$), equal to 123°C, indicates that a nanostructured transparent glass ceramic can be developed based on this glass [11].

The optical absorption spectrum of the glass (Fig. 2) was measured in the region 300 – 1100 nm with a CARY

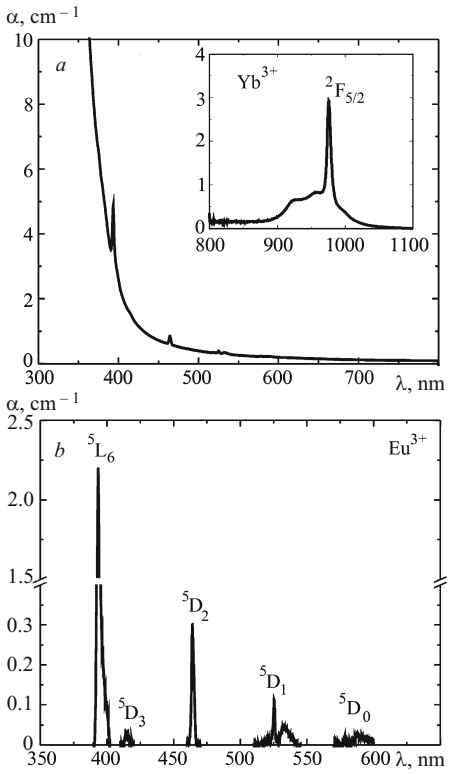

Fig. 2. Optical absorption spectrum of oxyfluoride glass, containing the ions Eu^{3+} and Yb^{3+}, in the system SiO_2–PbO–PbF_2–CdF_2: *a*) general form of the spectrum in the visible and near-IR region of the spectrum; inset) absorption band of ytterbium ions; *b*) structure of the absorption band of the Eu^{3+} ions (minus the 'gray' losses) and their interpretation.

Varian-5000 spectrophotometer. To interpret the absorption bands of Eu^{3+} ions the 'gray' losses due to light scattering were subtracted from the spectrum. The UV absorption edge of glass lies in the region about 350 nm. Bands which are associated with transitions from the ground state $^7F_0$ and the lower excited state $^7F_1$ into the higher lying excited state ^5D_J and are characteristic for trivalent europium ions Eu^{3+} are observed in the visible range of the spectrum. The strongest absorption band near 395 nm corresponds to the allowed transition $^7F_0 \rightarrow {}^5L_6$. The peak absorption coefficient for this band corresponds to 2.2 cm^{-1}. This is responsible for the high efficiency of the direct excitation of Eu^{3+} luminescence by InGaN-laser diodes.

The intense absorption in the region about 1 μm is due to the characteristic transition $^2F_{7/2} \rightarrow {}^2F_{5/2}$ for the ytterbium ions Yb^{3+}. Specifically, at the wavelength 960 nm of commercially available InGaAs laser diodes the absorption coefficient of the glass equals 0.8 cm^{-1}, which determines the 80% of the exciting light for a 2 mm thick sample. The efficiency of the excitation of ytterbium ions is less sensitive to the temperature-induced change in the wavelength of the laser-diode radiation because of the large width of the absorption band (see Fig. 2).

TABLE 1. Spectral position of the luminescence bands of oxyfluoride glass with direct excitation of Eu^{3+} ions at the wavelength 395 nm

Transition (Eu^{3+} ions)	Peak wavelength, nm	Wavelength, cm^{-1}
$^5D_1 \rightarrow {}^7F_2$	546	18,322
$^5D_0 \rightarrow {}^7F_0$	578	17,301
$^5D_0 \rightarrow {}^7F_1$	591	16,926
$^5D_0 \rightarrow {}^7F_2$	612	16,335
$^5D_0 \rightarrow {}^7F_3$	651	15,354
$^5D_0 \rightarrow {}^7F_4$	700	14,290

The luminescence of oxyfluoride glass with Eu^{3+} and Yb^{3+} ions was recorded in the spectral range 500 – 1100 nm with excitation by a commercial laser diode at wavelength 960 nm. A band due to the transition $^7F_{5/2} \rightarrow {}^2F_{7/2}$ was observed in the region about 1 μm. The decay time of the luminescence for this transition is 0.97 msec, which corresponds to the values for the best ytterbium laser glasses and indicates that the influence of nonradiative relaxation processes associated with defects and uncontrollable impurities as well as clusterization of active ions is weak. This confirms the high spectroscopic characteristics of the glass obtained.

Luminescence bands whose position corresponds to the radiation from Eu^{3+} ions with direct excitation at the wavelength 395 nm are observed in the visible region of the spectrum (Table 1).

This correspondence suggests that the Eu^{3+}ions are excited via the mechanism of cooperative energy transfer [12]. In this case, after a pair of close Yb^{3+} ions absorbs two photons with wavelength 960 nm the pair Yb^{3+}–Yb^{3+} in an intermediate 'virtual' state with energy $2E(^2F_{5/2})$ is formed. Next, electronic excitation energy is transferred from this pair to a single Eu^{3+} ion, the transition occurring in the state $^5D_1$ or $^5D_0$. Finally, radiative relaxation of Eu^{3+} ions is observed to occur from the metastable (long-lived state) $^5D_0$ into the lower-lying states $^7F_1$, $^7F_2$, $^7F_3$ and $^7F_4$ (Fig. 3).

The strongest luminescence band near 612 nm is related with the allowed transition $^5D_0 \rightarrow {}^7F_2$ and determines the color of the luminescence of the glass. The CIE color coordinates were determined in order to describe more accurately the color characteristics that are important from the standpoint of luminophores. For the glass obtained these coordinates are $x = 0.64$ and $y = 0.36$, which corresponds to a saturated orange-red color.

The high intensity of the orange-red luminescence of Eu^{3+} ions is related with the closeness of the energies for the 'virtual' state of the pair Yb^{3+}–Yb^{3+} and the energy of the excited states ^5D_J for the ion Eu^{3+}. It is mainly due to the corresponding choice of the oxyfluoride glass-forming system for synthesizing glass.

A series of bands (marked by the symbol *) associated with the up-conversion luminescence of the erbium ions Er^{3+} is present in the luminescence. Their presence is due to the

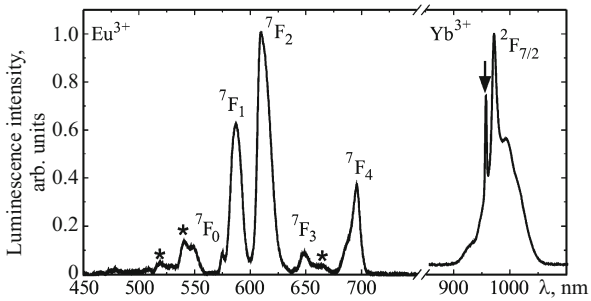

Fig. 3. Photoluminescence oxyfluoride glass containing Eu^{3+} and Yb^{3+} in the system SiO_2–PbO–PbF_2–CdF_2 with excitation at the wavelength 960 nm (marked by arrow) and its interpretation: * indicates up-conversion luminescence of the impurity ions Er^{3+}.

uncontrollable impurity ErF_3 in the reagent YbF_3 and is related with the technology of its production. At the same time the integral intensity for these bands does not exceed 2% of the intensity of Eu^{3+} bands. A particularity of the ytterbium glasses is clusterization of Yb^{3+} ions, which manifests in the light-blue luminescence near 480 nm. The integral intensity of this luminescence is extremely weak for the synthesized glass; this indicates that the distribution of the Yb^{3+} ions in the glass matrix is uniform.

The synthesized glass shows a significant potential for creating a nano-phase oxyfluoride glass ceramic containing lead fluoride PbF_2 nanocrystals whose crystal lattice incorporates the ions Eu^{3+} and Yb^{3+}. At the same time it has not been ruled out that cadmium ions Cd^{2+} also enter into PbF_2 lattice with the nanocrystals Eu, Yb:(Pb, Cd)F_2 being formed. At 300°C the PbF_2 crystals undergo a phase transition from the high-temperature cubic phase (β-PbF_2) into the low-temperature orthorhombic phase (α-PbF_2) [13]. The phase β-PbF_2 is chemically unstable at normal temperature and moisture content. At the same time it is this phase that is most attractive for optical applications. For this reason, by introducing this phase into the glass matrix by means of heat-treatment of the glass at temperatures above 300°C it is possible to overcome the problem of chemical instability and at the same time obtain a relatively large volume fraction of lead fluoride β-PbF_2 in the glass matrix. Specifically, preliminary experiments on heat treatment of the initial glass at temperatures 380 – 420°C indicate the formation of nanosize crystals Eu, Yb:(Pb, Cd)F_2.

New oxyfluoride glasses co-activated by europium and ytterbium ions and characterized by intense orange-red luminescence in the visible region of the spectrum were obtained in the course of these investigations. It was shown that the pair Yb^{3+}–Eu^{3+} in this glass matrix can be used to convert infrared laser radiation into visible light. It was proposed that the excitation of Eu^{3+} ions occurs via the mechanism of cooperative energy transfer. The synthesized glasses hold promise as a base for creating nano-phase up-conversion luminescing glass ceramic for up-conversion luminescing luminophores and solid-state lasers.

REFERENCES

1. L. A. Bueno, P. Melnikov, Y. Messaddeq, et al., "Er^{3+} and Eu^{3+} containing transparent glass ceramics in the system $PbGeO_3$–PbF_2–CdF_2," *J. Non-Cryst. Solids*, **247**, 87 – 91 (1999).
2. S. Ye, B. Zhu, J. Luo, et al., "Enhanced cooperative quantum cutting in Tm^{3+}–Yb^{3+} codoped glass ceramics containing LaF_3 nanocrystals," *Opt. Express* (2008).
3. L. Feng, J. Wang, Q. Tang, et al., "Optical properties of Ho^{3+}-doped novel oxyfluoride glasses," *J. Lumin*., **124**, 187 – 194 (2007).
4. M. J. Dejneka, "The luminescence and structure of novel transparent oxyfluoride glass-ceramics," *J. Non-Cryst. Solids*, **239**, 149 – 155 (1998).
5. M. Takahashi, M. Izuki, R. Kanno, et al., "Up-conversion characteristics of Er^{3+} in transparent oxyfluoride glass–ceramics," *J. Appl. Phys.*, **83**, 3920 (1998).
6. D. Chen, Y. Wang, Y. Yu, et al., "Structure and optical spectroscopy of Eu-doped glass ceramics containing GdF_3 nanocrystals," *J. Phys. Chem. C*, **112**, 18943 – 18947 (2008).
7. D. Chen, Y. Yu, P. Huang, et al., "Optical spectroscopy of Eu^{3+} and Tb^{3+} doped glass ceramics containing $LiYbF_4$ nanocrystals," *Appl. Phys. Lett*., **94**, 041909 (2009).
8. C. Bensalem, M. Mortier, D. Vivien, et al., "Optical investigation of Eu^{3+}:PbF_2 ceramics and transparent glass-ceramics," *Opt. Mater*., **33**, 791 – 798 (2011).
9. H. Scheife, G. Huber, E. Heumann, et al., "Advances in upconversion lasers based on Er^{3+} and Pr^{3+}," *Opt. Mater*., **26**, 365 – 374 (2004).
10. G. Dantelle, M. Mortier. G. Patriarche, et al., "Er^{3+}-doped PbF_2: Comparison between nanocrystals in glass-ceramics and bulk single crystals," *J. Solid-State Chem.*, **179**, 1995 – 2003 (2006).
11. R. S. Chalina, K. Annapurna, A. Tarafder, et al., "Luminescence and dielectric properties of nano-structured Eu^{3+}:K_2O–Nb_2O_5–SiO_2 glass-ceramics," *Solid State Sci.*, **11**, 1325 – 1332 (2009).
12. Y. Dwivedi, S. N. Thakur, and S. B. Rai, "Study of frequency upconversion in Yb^{3+}/Eu^{3+} by cooperative energy transfer in oxyfluoroborate glass matrix," *Appl. Phys. B*, **89**, 45 – 51 (2007).
13. A. B. Kulakov, A. A. Zhokhov, G. A. Emel'chenko, et al., "Growth of α-PbF_2 single crystals from aqueous solutions of inorganic acids," *J. Cryst. Growth*, **151**, 107 – 113 (1995).